Designation: C1636 – 13

Standard Guide for the
Determination of Uranium-232 in Uranium Hexafluoride[1]

1. Scope

1.1 This method covers the determination of ^{232}U in uranium hexafluoride by alpha spectrometry.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C787 Specification for Uranium Hexafluoride for Enrichment

C996 Specification for Uranium Hexafluoride Enriched to Less Than 5 % ^{235}U

C1163 Practice for Mounting Actinides for Alpha Spectrometry Using Neodymium Fluoride

C1284 Practice for Electrodeposition of the Actinides for Alpha Spectrometry

C1474 Test Method for Analysis of Isotopic Composition of Uranium in Nuclear-Grade Fuel Material by Quadrupole Inductively Coupled Plasma-Mass Spectrometry

D1193 Specification for Reagent Water

D3084 Practice for Alpha-Particle Spectrometry of Water

D3648 Practices for the Measurement of Radioactivity

2.2 *Other Standards*

DIN 25711 Determination of the ^{232}U isotopic content in uranium containing nuclear fuel solutions by α spectrometry.[3]

ISO 21847–3 Nuclear Fuel Technology—Alpha Spectrometry—Part 3: Determination of uranium-232 in uranium and its compounds.

3. Terminology

3.1 *Definitions:*

3.1.1 *region-of-interest (ROI)*—the channels, or region, in the alpha spectra in which the counts due to a specific radioisotope appear on a functioning calibrated alpha spectrometry system.

3.1.2 *Reagent blank*—DI water processed the same as the samples; used in the determination of the minimum detectable activity.

4. Summary of Guide

4.1 An aliquot of hydrolyzed uranium hexafluoride equivalent to 60 micrograms of uranium is converted to a nitric acid system and the uranium is extracted onto a solid phase extraction column. The daughters of uranium decay products are rinsed from the column and the uranium is then selectively eluted. The uranium is reduced and then coprecipitated with neodymium fluoride. Test Method C1163 provides further information on the use of neodymium fluoride to prepare actinide mounts for alpha spectrometry. The sample is then counted by alpha spectrometry, and the ^{232}U is calculated based on the observed activities of the uranium isotopes in the alpha spectra.

4.2 While this guide does not present details on electrodeposition as an alternative to neodymium fluoride precipitation for the preparation of a mount for alpha spectrometry Practice C1284 does present details on that option.

4.3 Alternate separation chemistry approaches may be found in the literature. It is the responsibility of the user of such alternative separation approaches to validate there effectiveness, especially the removal of potentially interfering thorium isotopes (section 6.1).

5. Significance and Use

5.1 The method is applicable to the analysis of materials to demonstrate compliance with the specifications set forth in Specifications C787 and C996. Some other specifications may be expressed in terms of mass of ^{232}U per mass of only ^{238}U (see ISO 21847–3:2007).

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[1] This guide is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Deutsches Institut für Normung e.V., Berlin, Germany (www.din.de).

6. Interferences

6.1 Incomplete removal of ^{228}Th could possibly interfere with the ^{232}U determination. Method DIN 25711 addresses the potential capability for this method to eliminate this potential interference.

6.2 Since only the relative amount of ^{232}U, relative to total uranium, is being determined in this method there is no impact to chemical loss in the separation or sample mounting chemistry. Therefore, unlike most alpha spectrometry methods, no yield tracer is necessary or useful.

6.3 The alpha emission energies of ^{235}U and ^{236}U are relatively close. Thus there is the potential for overlap of counts from one isotope into the ROI of the other. Where the alpha spectrometry system (section 7.1) provides spectral de-convolution algorithms may be used in the analysis of the spectra. Such de-convolution may allow for minimization of any possible bias in the reported results. However, it should be noted that these two isotopes typically account for a relatively small amount of the overall uranium mass. So any bias between the two should result in a relatively small overall bias in the reported ^{232}U result.

7. Apparatus

7.1 Alpha spectrometry system. See practices D3084 and D3648 for a description of the apparatus.

7.1.1 A ROI for each uranium isotope (^{232}U, ^{234}U, ^{235}U, ^{236}U, and ^{238}U) will need to be defined for the alpha spectrometry system being used. Based on these defined ROIs the fractional abundance of alpha decays within the energy range of the ROI for each isotope (AB_i in section 12.1) must be determined.

7.2 Ion Exchange Columns, able to hold a 10 mL resin bed and 15 mL solution washes.

7.3 Filter Paper, 0.1 µm pore size, 25-mm diameter, and compatible with HF.[4]

7.4 *Vacuum Funnel*—Polysulfone twist-lock with stainless steel screen for filter mounting.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades of reagents may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.[5]

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined in Specification D1193.

8.3 *Ammonium oxalate (0.1M)*—Dissolve 14.2 g $(NH_4)_2C_2O_4 \cdot H_2O$ in approximately 500 mL water and dilute to 1 litre.

8.4 *Ethanol*—Ethyl alcohol, absolute (200 proof), denatured.

8.5 *Hydrochloric acid (sp gr 1.19)*—Concentrated hydrochloric acid (HCl).

8.6 *Hydrochloric acid (9M)*—Add 750 mL concentrated HCl to 100 mL water and dilute to 1 litre.

8.7 *Hydrochloric acid (1.5M)*—Add 125 mL concentrated HCl to 500 mL water and dilute to 1 litre.

8.8 *Hydrochloric acid (1M)*—Add 83 mL concentrated HCl to 500 mL water and dilute to 1 litre.

8.9 *Hydrofluoric acid (minimum 48 % assay)*—Concentrated HF, reagent grade.

Warning—Severe burns can result from exposure of skin to concentrated hydrofluoric acid.

8.10 *Neodymium chloride (10 mg Nd/mL)*—Heat 25 mL of concentrated hydrochloric acid and 1.17 g of neodymium oxide on a hotplate until the neodymium oxide is in solution. Cool the solution and dilute to 100 mL with water.

8.11 *Neodymium chloride (100 µg Nd/mL)*—Dilute 1 mL of 10 mg Nd/mL solution to 100 mL with water.

8.12 Neodymium oxide (Nd_2O_3).

8.13 *Nitric acid (sp gr 1.42)*—Concentrated nitric acid (HNO_3).

8.14 *Nitric acid (3M)*—Add 188 mL concentrated nitric acid to 500 mL water and dilute to 1 litre.

8.15 *Oxalic acid in 1M HCl (0.1M)*—Dissolve 12.6 g $H_2C_2O_4 \cdot H_2O$ in 500 mL 1M HCl and dilute to 1 litre with 1M HCl.

8.16 *20 % Titanium Trichloride ($TiCl_3$) aqueous solution*—available as a 20 % (w/v) solution of titanium trichloride from commercial suppliers.

8.17 Extraction Chromatography Resin, containing octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (CMPO) dissolved in tri-n-butyl phosphate (TBP) as the immobilized extractant.[6]

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[4] Pall Life Sciences (formerly Gelman) Metricel filter has been found to be acceptable. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[5] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

[6] TRU resin from Eichrom Technologies Inc., Lisle, IL, USA, has been found to be acceptable. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend. Horwitz, E. P., Chiarizia, R., Dietz, M. L., Diamond, H., and Nelson, D., "Separation and Preconcentration of Actinides from Acidic Media by Extraction Chromatography," *Analytica Chemica Acta*, 281, 1993, pp. 361-372.

The Eichrom Technologies TRU resin is covered by a patent. Interested parties are invited to submit information regarding the identification of an alternative(s) to this patented item to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.

9. Hazards

9.1 Adequate laboratory facilities, such as fume hoods and controlled ventilation, along with safe techniques must be used in this procedure. Extreme care should be exercised in using hydrofluoric acid and other hot, concentrated acids. Use of rubber gloves is recommended.

9.2 **Warning—**Hydrofluoric acid is a highly corrosive acid that can severely burn skin, eyes, and mucous membranes. Hydrofluoric acid is similar to other acids in that the initial extent of a burn depends on the concentration, the temperature, and the duration of contact with the acid. Hydrofluoric acid differs from other acids because the fluoride ion readily penetrates the skin, causing destruction of deep tissue layers. Unlike other acids that are rapidly neutralized, hydrofluoric acid reactions with tissue may continue for days if left unattended. Due to the serious consequences of hydrofluoric acid burns, prevention of exposure or injury of personnel is the primary goal. Utilization of appropriate laboratory controls (hoods) and wearing adequate personal protective equipment to protect from skin and eye contact is essential. Acute exposure to HF can cause painful and severe burns upon skin contact that require special medical attention. Chronic or prolonged exposure to low levels on the skin may cause fluorosis.

10. Calibration and Standardization

10.1 The alpha spectrometry units should be calibrated for energy, resolution and efficiency according to the manufacturer's instructions. The background counting rate for the instrument should be measured at a frequency determined by the user. See Practices D3084 and D3648 for additional information.

11. Procedure

11.1 Pipette an aliquot of hydrolyzed uranium hexafluoride equivalent to 60 µg of uranium into a 150 mL beaker. Evaporate to dryness. Dissolve the residue with 10 mL 3M HNO_3 with gentle heating.

11.2 Condition a CMPO-TBP column by adding 5 mL 3M HNO_3.[7]

11.3 Add the sample from Step 11.1 to the CMPO-TBP column and allow it to pass through the column.

11.4 Rinse the CMPO-TBP column with 10 mL 3M HNO_3.

11.5 Rinse the CMPO-TBP column with 5 mL 9M HCl.

11.6 Rinse the CMPO-TBP column with 30 mL 1.5M HCl. This may be done with two 15-mL rinses.

11.7 Rinse the CMPO-TBP column with 15 mL 0.1M $H_2C_2O_4$ in 1M HCl.

11.8 Elute the uranium from the column with 20 mL 0.1M $(NH_4)_2C_2O_4 \bullet H_2O$ and collect in a PTFE beaker. If the alternative of electrodeposition (see Practice C1284) is to be used the eluent may be collected in a glass beaker instead.

11.9 Add 3 drops 20 % $TiCl_3$ aqueous solution, 0.75 mL of the 100 µg Nd/mL solution, and 1 mL concentrated HF to the uranium fraction. Swirl to mix then allow the sample to sit for 30 minutes. Standard Method C1163 should be consulted for additional information on preparing the neodymium fluoride mount for alpha spectrometry.

11.10 After placement of a 0.1 µm, 25-mm diameter filter on the vacuum funnel rinse first with ethanol and then water.

11.11 Add the uranium fraction to the filter and vacuum filter to dryness. Rinse the filter with water and filter to dryness. Rinse the filter with ethanol and filter to dryness. Dry the filter under a heat lamp.

11.12 Count the sample for an appropriate counting time in a calibrated alpha spectrometer (see Section 10.1).

12. Calculation of Results

12.1 Calculation of uranium isotope sample activity:

$$A_i = \frac{(G_i - B_i)}{(T \times E \times AB_i)} \qquad (1)$$

where:

A_i = activity of uranium isotope of interest (Bq) (i=232, 234, 235, 236, or 238),
G_i = gross counts in the analyte ROI accumulated in count duration T,
B_i = background counts in the analyte ROI accumulated in count duration T,
AB_i = abundance of alpha decay of uranium isotope of interest in defined ROI (section 7.1.1), expressed as a fraction,
E = detector alpha counting efficiency (cps/dps), and
T = counting duration, s.

Additional calculations, including reagent blank subtraction, can be found in Practice D3084.

12.2 Calculation of the *a priori* Minimum Detectable Activity (MDA) for the uranium isotope of interest[8]

$$MDA_i = \frac{(4.65 \times S_b + 2.71)}{(E \times T \times AB_i)} \qquad (2)$$

where:

MDA_i = minimum detectable activity (MDA) (Bq) for uranium isotope of interest, and
S_b = standard deviation of the background counts.

12.3 Conversion of activity to mass:

$$W_i = \frac{A_i}{SA_i} \qquad (3)$$

where:

W_i = weight of uranium isotope of interest (µg),
SA_i = specific activity of uranium isotope (Bq/µg),

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[7] The 2 mL prepacked TRU column from Eichrom Technologies Inc. has been found to be acceptable. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

[8] Curie, L.A., "Limits of Qualitative Detection and Quantitative Determination," *Analytical Chemistry*, vol. 40, no.3, pp. 586-593, 1968.

SA_{232} = 792000 Bq/µg,[9]
SA_{234} = 231 Bq/µg,
SA_{235} = 0.07995 Bq/µg,
SA_{236} = 2.4 Bq/µg, and
SA_{238} = 0.0124 Bq/µg.

An alternative approach to determining the relative mass contributions of ^{234}U, ^{235}U, ^{236}U, and ^{238}U is using a mass spectrometry method such as Test Method C1474.

12.4 Calculation of concentration of ^{232}U:

$$C_{232} = \frac{W_{232}}{\left(\sum W_i \times 1000000\right)} \tag{4}$$

where:

C_{232} = concentration of ^{232}U (µg/g U).

13. Keywords

13.1 Alpha spectrometry; ion exchange column; mass spectrometry; solid phase extraction; specific activity; uranium-232; uranium hexafluoride

APPENDIXES

(Nonmandatory Information)

X1. Precision and Bias

X1.1 This analytical method does not have sufficient data to be qualified as a Standard Method for ASTM but is offered as a Guide for those wishing options for the analysis of ^{232}U in uranium hexafluoride. At present there are no Certified Reference Materials available from a national standards body to provide a complete Precision and Bias statement, however the information below is offered as an example of data produced following this Guide.

X1.2 Twenty samples of uranium hexafluoride were spiked at the 0.00125 µg ^{232}U per gram of uranium level and analyzed to determine precision and bias. The relative standard deviation of the 20 results was 15 % as an indication of precision. The percent recovery was 103 % as an indication of bias.

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[9] Specific activities calculated from data in International Commission on Radiological Protection (ICRP) Publication 38, "Radionuclide Transformations: Energy and Intensity of Emissions," *Annals of the ICRP*, Vol 11-13, 1983. Alternate specific activities are acceptable.

X2. Alpha Emission Energies and Abundances

X2.1 See Table X2.1.

TABLE X2.1 Emission energy and abundance of major alpha emissions of select isotopes[A]

Uranium isotope	Energy, keV	Abundance, %
^{232}U	5139.0 ± 2.0	0.30 ± 0.02
	5263.36 ± 0.09	31.55 ± 0.23
	5320.12 ± 0.14	68.15 ± 0.23
^{234}U	4603.5 ± 1.5	0.20 ± 0.01
	4722.4 ± 1.4	28.42 ± 0.09
	4774.6 ± 1.4	71.38 ± 0.16
^{235}U	4150 ± 5	0.9 ± 0.2
	4214.7 ± 1.9	5.7 ± 0.6
	4219 ± 6	~0.9
	4271 ± 5	~0.4
	4366.1 ± 2.0	17 ± 2
	4397.8 ± 1.3	55 ± 3
	4414 ± 4	2.1 ± 0.2
	4435 ± 5	~0.7
	4502 ± 2	1.7 ± 0.2
	4556 ± 2	4.2 ± 0.3
	4596.4 ± 1.3	5.0 ± 0.5
^{236}U	4332 ± 8	0.26 ± 0.01
	4445 ± 5	25.9 ± 4.0
	4494 ± 3	73.8 ± 4.0
^{238}U	4151 ± 5	20.9 ± 2.7
	4198 ± 3	79.0 ± 2.7

[A] S.Y.F. Chu, L.P. Ekström and R.B. Firestone, "WWW Table of Radioactive Isotopes," database version 2/28/99, Available http://ie.lbl.gov/toi/, February 2004.

X3. Sensitivity

X3.1 Specifications C787 and C996 have limits for ^{232}U as low as 0.0001 µg/g U. Based on the parameters presented in Table X3.1 a ^{232}U concentration of 0.00006 µg/g U can be determined using the method presented in this guide.

TABLE X3.1 Analysis parameters for conservative calculation of method sensitivity.

Parameter	Value
^{232}U ROI background	0.005 counts/60 seconds
Alpha counting efficiency, fractional	0.20
Count duration, seconds	86,400
^{232}U ROI sample count rate/background	5
Uranium chemical recovery, fractional	0.75

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